

Flammability Properties of Phosphine Oxide Copolymers and of Commodity Polymers with New Flame Retardant Additives

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ABSTRACT

Several different phosphine oxides, triphenylphosphine oxide, diphenylphosphine oxide, and trihydroxylpropylphosphine oxide, are added into nylon 6,6 by copolymerization and by blending. The flammability properties of these samples are measured in the Cone Calorimeter. The results show that the addition of any of these phosphine oxides to nylon 6,6 reduces the heat release rate significantly but increases the amount of CO and soot particles. Although small amounts of char are formed with the phosphine oxides, the flame retardant site appears to be mainly in the gas phase. No significant difference in flammability properties is observed between the copolymer samples and the blended sample. A small quantity of silica gel with K_2CO_3 as an additive reduces heat release rate of many different polymers and forms carbonaceous char for PP, PMMA, nylon 6,6 and also significantly enhances char yields of cellulose and PVA. The solid-state NMR data of char formed from PVA with silica gel/ K_2CO_3 show increase in aromaticity in the char compared with in the char generated from PVA only.

1. Introduction

Today, synthetic polymeric materials are rapidly replacing more traditional materials such as steel and nonferrous metals and natural polymeric materials such as wood, cotton, natural rubber, and so on, but they also are materials in their own right, possessing uniquely valuable physical properties. However, one weak aspect of polymeric materials compared with steel and other metals is that these materials are combustible under certain conditions. Thus, many polymer-containing end products (for example, cables, carpets, furniture) must pass some type of regulatory test to help assure public safety from fire.

The fire safety of materials can be significantly enhanced by increased ignition resistance, reduced flame spread rates, reduced heat release rates, and reduced amounts of toxic and smoke products, preferably *simultaneously*. The use of more thermally stable polymers, of which many are available, might be a valid solution to these requirements but generally the cost of these materials is relatively high and, furthermore, their physical properties or processability may not be as desirable as those of less stable polymers. The most common approach to enhance fire safety performance is the use of flame retardant additives in large volume commodity polymers. The

additives must have a minimum impact on physical properties and product cost. Although halogenated flame retardants are highly effective for reducing the heat release rate of commodity polymers, public perception of the environmental impact of recycling and incineration of certain halogenated flame retardants has become an issue in Europe [1,2]. Furthermore, concern over possible corrosion damage to metals by the combustion products from fire in which plastics containing halogenated groups or additives are involved, may impact the use of halogenated compounds. As our society becomes more dependent on high technology, the corrosion threat from fire in communication and electronic systems could become a problem.

Therefore, this study aims at developing other types of flame-retardant treatments. One possible alternative is the use of phosphorous based compounds whose effective flame retardant performance is well known [3,4]. However, it appears that the mechanism of flame retardancy depends on the polymer resin. It has been reported that the flame retardant operates in the condensed phase by forming char for rigid polyurethane [5] but, for polystyrene, phosphorous flame retardants act primarily in the gas phase [6]. To determine flame retardant effectiveness of phosphine oxides, various hydrolytically stable aromatic phosphine oxides were chemically incorporated into nylon 6,6, PET, and epoxy polymers. Their flammability properties were measured in the Cone Calorimeter. Another flame retardant approach used in this study is through the formation of char. There are several mechanisms whereby the formation of char reduces flammability: (1) part of the carbon (and hydrogen) stays in the condensed phase, thus reducing the amount of gaseous combustible degradation products evolved; (2) the low thermal conductivity of the char layer over the exposed surface acts as thermal insulation to protect the virgin polymer beneath [7]; and (3) a dense char acts as a physical barrier to gaseous combustible degradation products [8]. The majority of commodity polymers do not form char during their combustion and current research seeks to determine how to form char from these polymers. This char forming approach is most successful when the polymer chars rapidly and early in the burning process. To be useful the charring process must be designed so that it occurs at a temperature greater than the processing temperature but before the polymer decomposition has proceeded very far. Our approach to char promotion is to investigate relatively inexpensive additives which form char from commodity polymers and to gain a fundamental understanding of the additive's char formation mechanism with the goal of optimizing the additive's performance. Recent studies of the flammability of polymers containing silicon based materials have shown these materials to be promising fire retardants, either as additives, in blends with organic polymers or in copolymers [9,10]. We have selected a combination of silica gel and potassium carbonate additives and determined their effects on flammability properties of commodity polymers[11].

2. Experimental

All phosphine oxide copolymers were synthesized at Virginia Polytechnic Institute and State University and the synthetic methods used are described in refs. 13-15. The chemical structure of the copolymer of triphenylphosphine oxide with nylon 6,6 is shown in Fig.1. Samples were prepared by compression molding and their size was 10 cm square with about 3 mm thickness.

Polymers and additives used for the formation of char in this study were* silica gel (Fisher Scientific Co., 28-200 mesh), potassium carbonate, K_2CO_3 (Mallinckrodt, granular) polypropylene, PP (Scientific Polymer Products, Inc., $M_w = 240,000$ g/mole), polystyrene, PS (Scientific Polymer Products, Inc., $M_w = 45,000$ g/mole), styrene-acrylonitrile, SAN (GE Polymers), poly(methymethacrylate), PMMA (Du Pont, Elvacite), poly(vinyl alcohol), PVA (Scientific Polymer Products, Inc., $M_n = 86,000$ g/mole, $M_w = 178,000$ g/mole, 99.7% hydrolysed via NaOH aqueous method), nylon 6,6 (Rhone Poulenc) and alpha cellulose (Sigma Chemical Co., fiber, 99.5%). All were used as received. The additives were mixed with the polymers by grinding the powders together in a mortar and pestle (generally, the total additive mass percentage was at most 10%). Cone samples were prepared by compression molding the powdered samples (40 g-55 g) into 75 mm x 7-8 mm disks using a Carver press with a heated mold (~ 22 MPa (10 tons) held for 3-5 minutes at 150 °C or at glass transition temperature).

The flammability properties of these samples were measured by the Cone Calorimeter (ASTM E1354) at external flux of either 35 kW/m² or 40 kW/m² in air. The sample was wrapped in a thin aluminum foil except the irradiated sample surface and mounted horizontally on a Marinite board (calcium silicate) as an insulation material. A heavy metal container used in the standard test procedure was not used in this study to avoid heat loss to the container.

3. Results and Discussion

3.1 Phosphine Oxide Copolymers

The effect of incorporation of triphenylphosphine oxide, TPO, into nylon 6,6 as a copolymer on the heat release rate is shown in Fig.2 for three different levels of phosphine oxide from 10 mol% to 30 mol%. A significant decrease in heat release rate is observed as the amount of the triphenylphosphine oxide comonomers is increased. Piloted ignition delay time decreases slightly with increasing amount of the triphenylphosphine oxide. This is consistent with the slight decrease in the onset of thermal degradation temperature (from 410 °C for nylon 6,6 to 402 °C for the 30 mol% of the phosphine oxide sample [14]) seen in the TGA data (thermal gravimetric analysis) in air. The mass burning rate is calculated from the transient sample weight divided by the initial sample surface area and the results are shown in Fig.3. The mass loss rate decreases with the amount of the triphenylphosphine oxide but this trend is much less than that of the heat release rate. The heat of combustion, ΔH_c , is calculated from the transient heat release rate divided by the transient mass loss rate at the same instance. The ΔH_c results shown in Fig. 4 indicates that the heat of combustion decreases with increase in triphenylphosphine oxide. A 40% reduction in the heat of combustion is about 40% from nylon 6,6 to the copolymer of triphenylphosphine oxide (30 mol%) and nylon 6,6. However, the yield of char after the test is from 2.3 ± 0.2 % for nylon 6,6 to 8.7 ± 0.8 % for the copolymer sample. These trends indicate that there is some flame retardant activity in the condensed phase but it appears the majority of

* Certain commercial equipment, instruments, materials, services or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.

the flame retardant activity is in the gas phase. This is confirmed by significant increases in CO yield and specific extinction area, shown in Figs. 5 and 6, respectively. The specific extinction is calculated from the extinction measurement of a He-Ne laser beam passing through the exhaust duct of the Cone Calorimeter divided by the volume flow rate in the duct and the transient mass loss rate. This value indicates the concentration of soot particulates generated by the combustion of the sample. Since the effect of the triphenylphosphine oxide on the mass loss rate is relatively small, as shown in Fig.3, the overall rate of CO and soot particles formation increased with an increase in the phosphine oxide content in the copolymer sample. The flammability properties of these samples are summarized in Table 1. A small increase in char yield (from 0% to 8.5%) with an increase in the triphenylphosphine oxide is also observed in the TGA study in at 750 °C [14]. Although the physical properties of the copolymer tends to be better than that of the blended sample, the cost of the copolymer sample might be higher than that of the blended sample. Another flammability study was carried out to compare the flame retardant effectiveness of the copolymer and a blend material. Triphenylphosphine oxide (10 mol%) was blended with nylon 6,6 and the flammability properties of this blend are compared with those of nylon 6,6 and of the nylon 6,6/TPO copolymer. The comparison of heat release rate among the three samples is shown in Fig.7. The heat release rate of the blended sample does not differ significantly from that of the copolymer but the ignition delay time of the blended sample tends to be shorter than that for the copolymer sample. There are no significant difference in burning rate, heat of combustion, CO and specific extinction area. These results indicate that the flammability properties of nylon 6,6 with triphenylphosphine oxide as a blend or as a copolymer are not significantly different. Other copolymers based on polycarbonate, PET, and epoxy (Epon 828) with triphenylphosphine oxide were synthesized to examine the effects of polymer chemical structure on flame retardant effectiveness of the phosphine oxide. The results are similar to those for nylon 6,6. The heat release rates of these polymers are reduced by the incorporation of triphenylphosphine oxide as a copolymer but an increase in the amount of CO and soot particulates was also observed.

The increase in the formation of soot particulates and CO, by the incorporation of triphenylphosphine oxide, could be caused by the combustion of pendant benzene groups from triphenylphosphine oxide. When benzene is a part of the polymer backbone, it tends to participate in formation of char [16]. However, pendant benzene groups do not always promote char formation. This is the case in polystyrene where the pendant benzene groups tend to generate soot particulates instead of char. In order to confirm this hypothesis, a new copolymer sample was synthesized with the pendant benzene replaced with methyl. The heat release rate of copolymer samples of diphenylphosphine oxide, DPO, with nylon 6,6 is not significantly different from that of copolymer samples of triphenylphosphine oxide with nylon 6,6 as shown in Fig.8. The mass loss rate, heat of combustion, CO yield, and specific extinction area of copolymer samples of diphenylphosphine oxide/nylon 6,6 are not significantly different from those of copolymer samples of triphenylphosphine oxide/nylon 6,6. These results indicate that the pendant benzenes do not enhance the formation of CO and soot particulates. To determine if benzene in the copolymer backbone was contributing to the increase in CO and soot particulates, we examined an aliphatic phosphine oxide blended with nylon 6,6. Trihydroxypropylphosphine oxide, THPPO, was used as the aliphatic phosphine oxide. The blended sample has 30 weight% of THPPO. The

heat release rate of the blended sample with THPPO is compared with that of nylon 6,6 sample (This nylon 6,6 is a commercial sample whose thermal degradation characteristic might be different from that of the nylon 6,6 sample used for the copolymer study.). The results, shown in Fig.9 at an external flux of 35 kW/m^2 , show a significant reduction in heat release rate similar to the copolymer samples with TPO. In addition, the specific extinction area of the blended sample is much higher than that of nylon 6,6, as shown in Fig.10. The char yield of the blended sample was 4.2 %. These results are similar to those of the copolymer samples with TPO. The results suggest that phosphorous is the major factor in controlling the reduction of the heat release rate and the increase in CO and soot particulates. There is evidence to suggest the contention that, if phosphorous is released into the gas phase, it acts as a radical scavenger of H-atoms [17, 18]. On the other hand, the measurable char yield in the tested sample suggests that there is some activity in the condensed phase. If phosphorous stays in the condensed phase during combustion, phosphorous could be a significant char forming flame retardant.

3.2 Silica gel

The intention in using silica gel with K_2CO_3 was to devise a method of in-situ formation of silicon based fire retardants during combustion. The reaction of silica gel and organic alcohols in the presence of metal hydroxides has been shown to give multicoordinate organosiliconate compounds [12]. Instead of synthesizing these materials and then combining them with various polymers to evaluate their effect on polymer flammability properties, we envisioned the reaction occurring in the condensed phase of the pyrolyzing polymer beneath the burning surface, by combining a polyhydroxylic polymer, e.g. PVA or cellulose, with silica gel and K_2CO_3 . If the reaction between the polymer and the additives occurs, it should crosslink the polymer and might assist in forming a silicon-oxy-carbide, SiOC, type protective char during combustion. The flammability properties of these samples were measured in the Cone Calorimeter at an incident flux of 35 kW/m^2 . The results are summarized in Table 2 for the polymers and polymers with the addition of silica gel and K_2CO_3 [19]. Assuming all additives remained in the polymer residue after the test, the char yield was determined as (polymer residue weight - initial additives weight)/initial mass of polymer in the sample. The results show that the additives enhance the formation of carbonaceous char even if the original polymer does not generate any char such as PP, PS and PMMA. The increases in carbonaceous char yield for PVA and cellulose is nearly a factor of 10. As discussed in the Introduction Section, the intention in using silica gel with K_2CO_3 was to devise a method of in-situ formation of silicon based crosslinks to enhance formation of char. The reaction of silica gel and organic alcohol in the presence of metal hydroxides has been shown to give multicoordinate organosiliconate compounds [12]. Therefore, it is not surprised by the significant increase in char yield for PVA and cellulose. It was not expected to form char for PP and PS which do not have any alcohol groups in their polymer structure. The reduction in peak heat release rate by the additives is quite significant, reaching about 50% for PP, PVA, cellulose, and nylon 6,6. A typical result for the reduction in heat release rate is shown in Fig.11 for PP. However, the heat of combustion is not significantly affected by the additives and also the concentrations of particulates, shown in Fig.12, and CO in the combustion products do not increase with the additives. These trends are significantly different from those for halogenated flame retardant additives or even for above described

copolymer samples of phosphine oxide. The results presented here clearly demonstrate that the flammability of a wide variety of polymers is dramatically reduced in the presence of relatively small concentrations of silica gel and K_2CO_3 . However, we have only just begun to find the effects of the additives on flammability. We are planning to evaluate other types of basic materials (K_2CO_3 is hygroscopic) and the effects of particle size, internal pore size and silanol content of the silica gel on flammability.

The above results indicate that these additives appear to act in the condensed phase. In order to understand their effects on polymer pyrolysis, the chars of PVA with silica gel / K_2CO_3 (90:6:4) and PVA with silica gel only (90:10) isolated following combustion in the Cone calorimeter, were analyzed using several solid state ^{13}C NMR techniques. The spectra are shown in Figures 13 and 14 for the PVA with silica gel only (90:10) char and for the PVA with silica gel / K_2CO_3 (90:6:4) char, respectively. The normal CP/MAS ^{13}C NMR, shown in the middle of Figure 11, contains a broad resonance in the aromatic-olefinic region from 110 ppm to 150 ppm and two weaker broad signals in the aliphatic region, one centered at 20 ppm and the other at 35 ppm. This spectrum shows that the ratio of aromatic-olefinic (sp^2) carbon to aliphatic (sp^3) carbon is $\sim 3:1$. An interrupted decoupling (ID)-CP/MAS spectrum of this char, shown in the bottom spectrum in Figure 9, reveals only the non-protonated carbons which have cross-polarized. Comparison of the ID-CP/MAS spectrum (bottom) to the normal CP/MAS spectrum (middle) reveals that the downfield shoulder in the CP/MAS spectrum, centered at 135 ppm, is due to non-protonated aromatic-olefinic carbons. The result of subtracting the appropriate intensity of the ID-CP/MAS spectrum from the CP/MAS spectrum, so that the downfield shoulder is removed, is shown in the top of Figure 13. This difference spectrum (top) reveals that the narrower upfield portion of the aromatic-olefinic resonance, at 110 ppm -135 ppm, is due to protonated carbons. The ratio of non-protonated to protonated aromatic-olefinic carbons in the cross-polarized signal of this char sample is approximately 1 to 1. Comparison of the set of NMR data above with that for the char resulting from the pyrolysis of pure PVA reveals that the non-protonated to protonated aromatic-olefinic carbon ratio is 1:1 in both cases and that the chars appear to have almost identical structure [19]. However, the presence of silica gel in PVA reduces the peak heat release rate from 609 kW/m^2 , for pure PVA, to 250 kW/m^2 . The presence of silica gel also increases the char yield from 5% to 27%. It appears that the silica gel does not change the type of char formed, since the chars have similar structure, but it does change the rate at which it forms since the char yield is higher and the flammability is lower.

A similar series of spectra of the char from PVA with silica gel and K_2CO_3 (90:6:4) is shown in Figure 14. The normal CP/MAS spectrum (middle) contains the sharp carbonate resonance at 162 ppm and a broad resonance in the aromatic-olefinic region from 115 ppm to 150 ppm. In contrast to the spectra for PVA only or for PVA with silica gel (10%) there is little evidence of any aliphatic (sp^3) carbon. Comparison of the ID-CP/MAS spectrum (bottom) to the normal CP/MAS spectrum (middle) reveals, as was observed for pure PVA and for PVA with silica gel, that the downfield shoulder in the CP/MAS spectrum, centered at 135 ppm, is due to non-protonated aromatic-olefinic carbons. The result of subtracting the appropriate intensity of the ID-CP/MAS spectrum from the CP/MAS spectrum, so that the downfield shoulder is removed, is shown in the top of Figure 10. The difference spectrum (top) reveals that the upfield portion of

the aromatic-olefinic resonance, at 115 ppm -135 ppm, is due to protonated carbons. The ratio of non-protonated to protonated aromatic-olefinic carbon in the spectrum of this char sample is approximately 1.5 to 1, i.e., this char contains a greater fraction of non-protonated aromatic-olefinic carbons than the char formed in the absence of K_2CO_3 . To the extent that the cross-polarized signals in these materials reflect the sample-wide chemistries, these data indicate that the presence of the K_2CO_3 has increased the extent of carbon-carbon bond formation and therefore of crosslinking in the char. This may be the reason for the even lower flammability (peak heat release rate: 609 kW/m² for pure PVA; 250 kW/m² for PVA with silica gel; and 194 kW/m² for PVA with silica gel and K_2CO_3) and for the higher char yield in the presence of K_2CO_3 (char yield: 5% for pure PVA; 27% for PVA with silica gel; and 43% for PVA with silica gel and K_2CO_3).

We are also characterizing the residues formed from the combustion of the polymers discussed above using solid state 1H , ^{29}Si , single pulse (more quantitative) ^{13}C NMR, and other techniques. Our recent ^{29}Si NMR measurement of the carbonaceous char of PVA in the presence of the additives showed no signal corresponding to presumed Si-O-C or Si-C bonds. Therefore, it is not clear at present how silica gel and K_2CO_3 enhance the formation of carbonaceous char from a wide variety of polymers.

4. Summary

It appears that phosphorous in phosphine oxides, such as triphenylphosphine oxide, diphenylphosphine oxide and trihydroxylpropylphosphine oxide, manifests its flame retardant activity mainly in the gas phase during combustion of nylon 6,6, PET, polycarbonate and epoxy (Epon 828). It reduces heat release rate but increases the formation of CO and soot particulates. There are no significant difference between blending and copolymerization of the phosphine oxides into the polymer samples. The use of silica gel as an additive to various polymer samples generates char even though the original polymers do not form any char. This approach reduces heat release rate without increasing CO and soot particulates. It appears that the combination of silica gel with K_2CO_3 enhances the formation of char possibly as a catalyst. However, the detailed chemical or physical mechanism of the char formation by silica gel is not understood.

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Sample	Peak heat release rate (kW/m ²)	Total heat release (MJ/m ²)	Heat of combustion (MJ/kg)	Char yield (%)	CO yield (%)	Specific extinction area (m ² /kg)
nylon 6,6	1190 ± 150	95 ± 10	31 ± 3	2.3 ± 0.2	1.4 ± 0.2	177 ± 30
nylon 6,6+ TPO(10 %)	930 ± 120	72 ± 7	25 ± 2	6.1 ± 0.6	10 ± 1.5	700 ± 100
nylon 6,6 + TPO(20 %)	610 ± 90	62 ± 6	21 ± 2	7.5 ± 0.7	15 ± 2	1120 ± 150
nylon 6,6 + TPO(30 %)	490 ± 70	50 ± 5	18 ± 2	8.7 ± 0.8	16 ± 2	1480 ± 200

Table 1. Effects of TPO incorporation on the flammability properties of nylon 6,6 at an external radiant flux of 35 kW/m².

Sample disk: 75mm x 8mm	Char Yield (%)	LOI (%)	Peak HRR (Δ) (kW/m ²)	Mean HRR (kW/m ²)	Mean Heat of Combustion (MJ/kg)	Total Heat Released (MJ/m ²)	Mean Specific Ext. Area (m ² /kg)	Mean CO yield (kg/kg)
PP	0	-	1,761	803	38	357	689	0.04
PP w/ 6%SG & 4%PC	10	-	736 (58%)	512	33	297	710	0.04
PS	0	18	1,737	1,010	25	277	1,422	0.07
PS w/ 6%SG & 4%PC	6	24	1,190 (31%)	725	25	246	1,503	0.07
PMMA	0	18	722	569	23	319	210	0.01
PMMA w/ 3%SG & 1%PC	15	25	420 (42%)	246	21	231	199	0.05
PVA	4	-	609	381	17	221	594	0.03
PVA w/ 10%PC	9	-	322 (47%)	222	17	145	571	0.03
PVA w/ 10%SG	29	-	252 (57%)	173	15	131	361	0.03
PVA w/ 3%SG & 1%PC	16	-	295 (52%)	232	16	166	447	0.03
PVA w/ 6%SG & 4%PC	43	-	194 (68%)	114	12	101	201	0.03
Cellulose	4	-	310	161	11	101	27	0.02
Cellulose w/ 6%SG & 4%PC	32	-	149(52%)	71	5.3	34	20	0.04
SAN	2	-	1,499	837	25	197	1,331	0.07
SAN w/ 6%SG & 4%PC	3	-	1,127 (25%)	772	23	169	1,301	0.06
Nylon 6, 6	1	30	1,131	640	23	108	234	0.02
Nylon 6, 6 w/ 4%PC	3	-	854 (25%)	570	25	103	342	0.03
Nylon 6, 6 w/ 6%SG	4	-	558 (51%)	365	24	111	164	0.02
Nylon 6, 6 w/ 3%SG & 2%PC	5	33	526 (53%)	390	22	105	171	0.02
Nylon 6, 6 w/ 6%SG & 4%PC	6	30	546 (52%)	370	24	102	185	0.02

Incident heat flux = 35 kW/m² ; SG = Silica Gel; PC = K₂CO₃

Table 2. Flammability properties of various polymers with silica gel and potassium carbonate in Cone Calorimeter and in Limiting Oxygen Index test. Uncertainties in peak heat release rate and in mean extension area are $\pm 15\%$ and those in all other quantities are $\pm 10\%$.

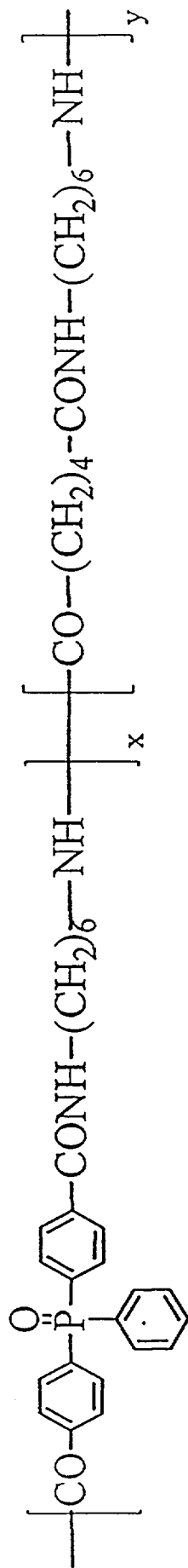


Fig.1 Copolymer chemical structure of Nylon 6,6/TPO

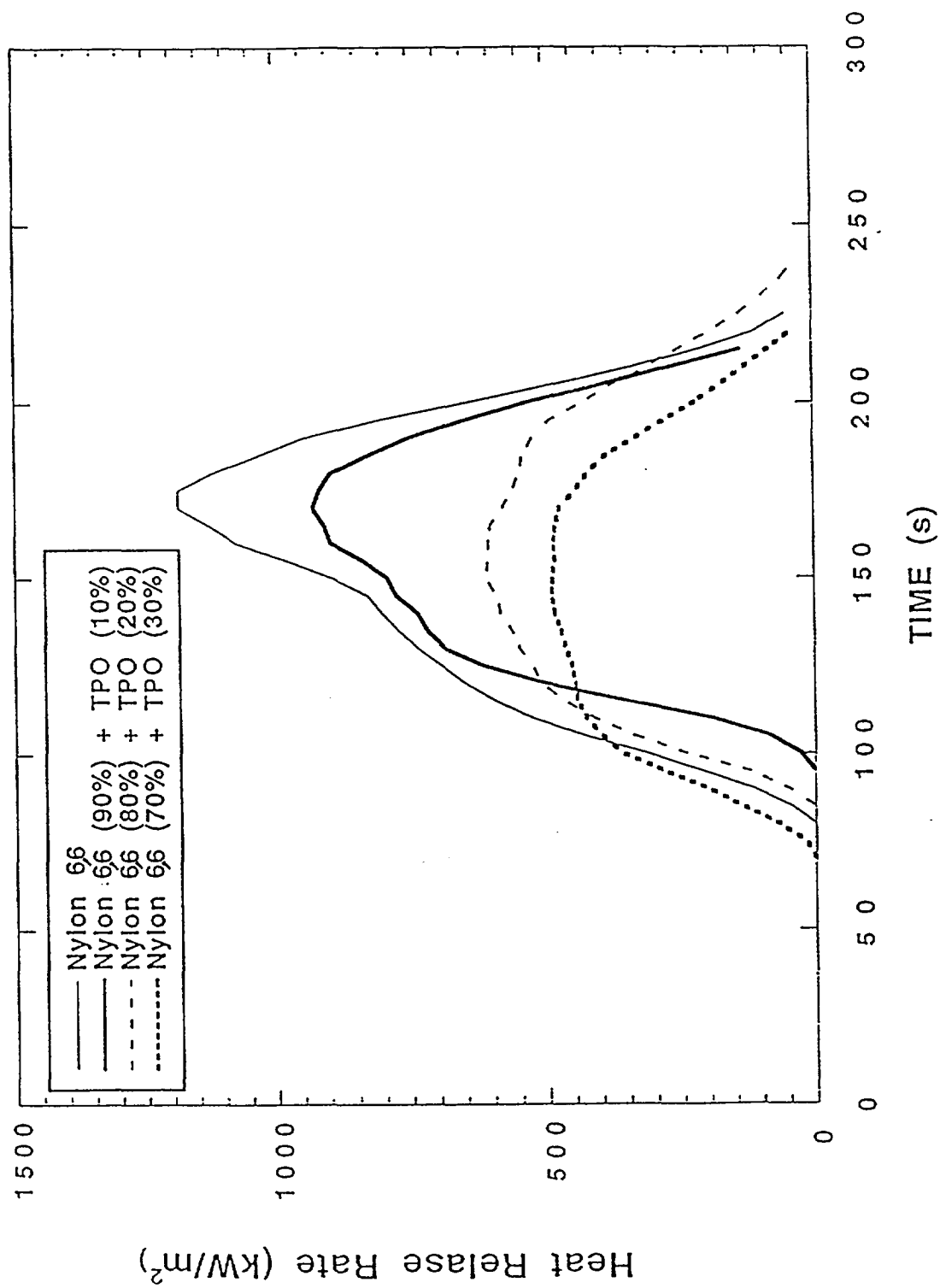


Fig.2 Comparison of heat release rate of nylon 6,6 and copolymer samples of nylon 6,6/TPO at external flux of 40 kW/m².

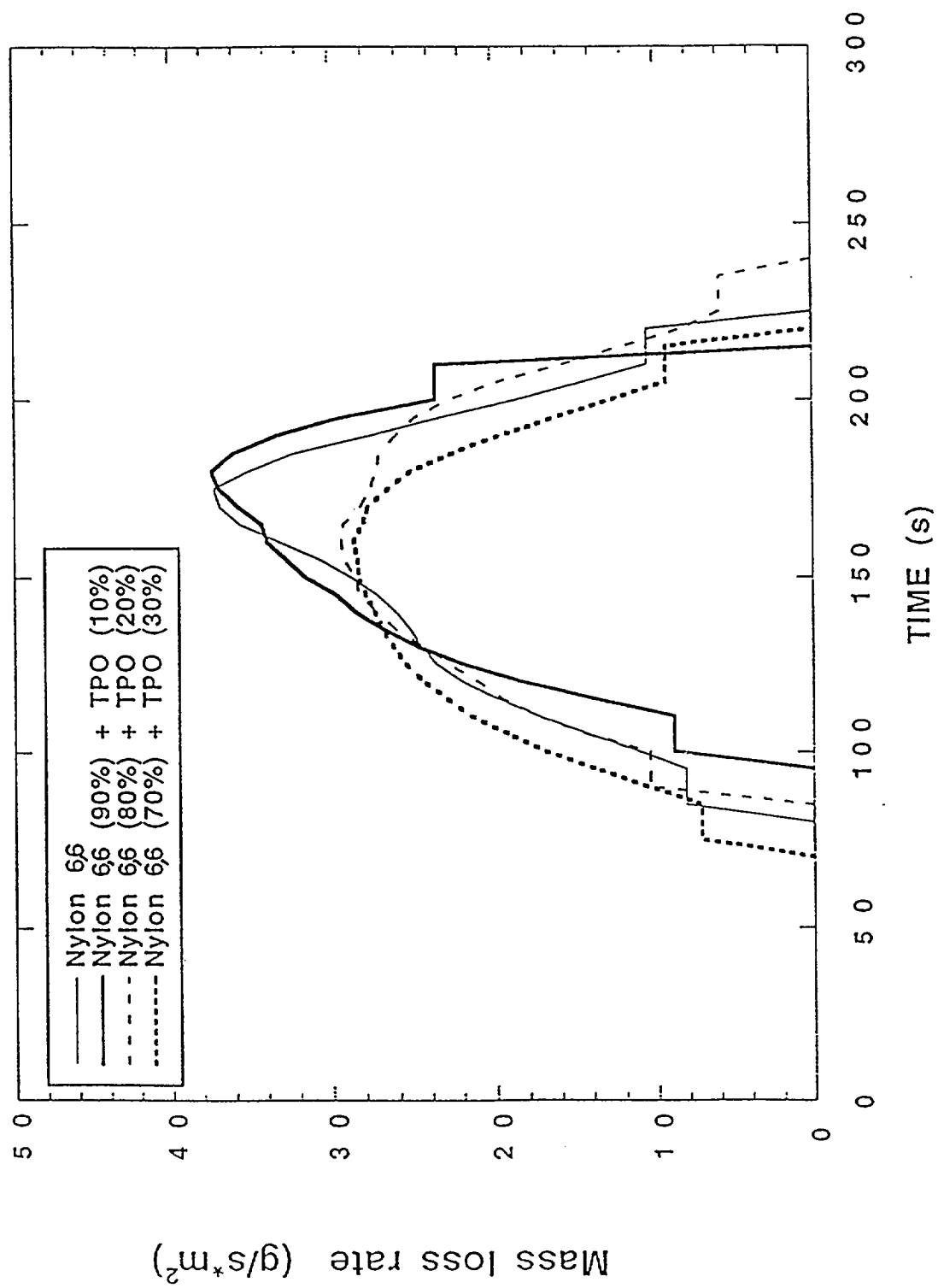


Fig.3 Comparison of mass loss rate of nylon 6,6 and copolymer samples of nylon 6,6/TPO at external flux of 40 kW/m².

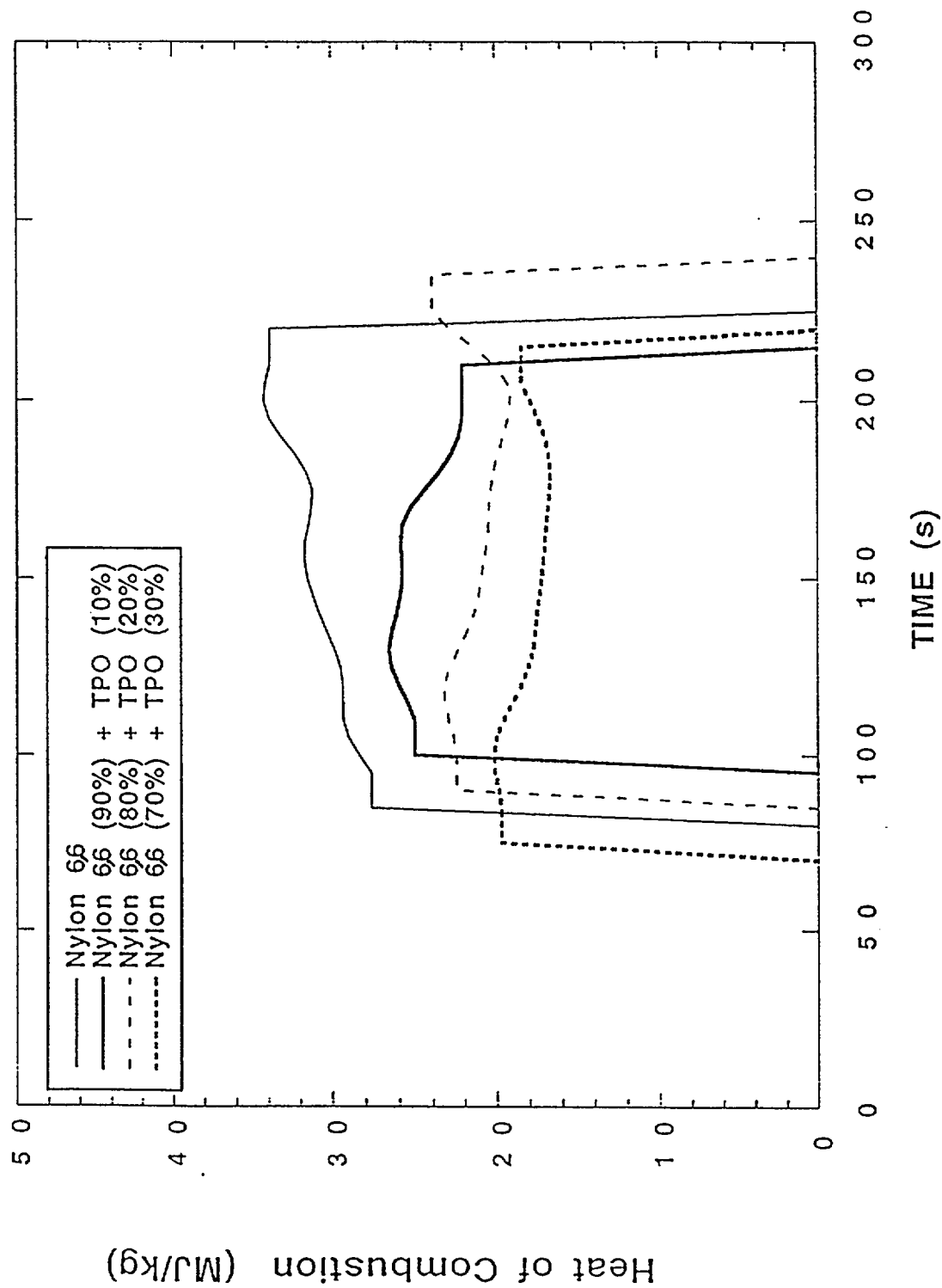


Fig.4 Comparison of heat of combustion of nylon 6,6 and copolymer samples of nylon 6,6/TPO at external flux of 40 kW/m².

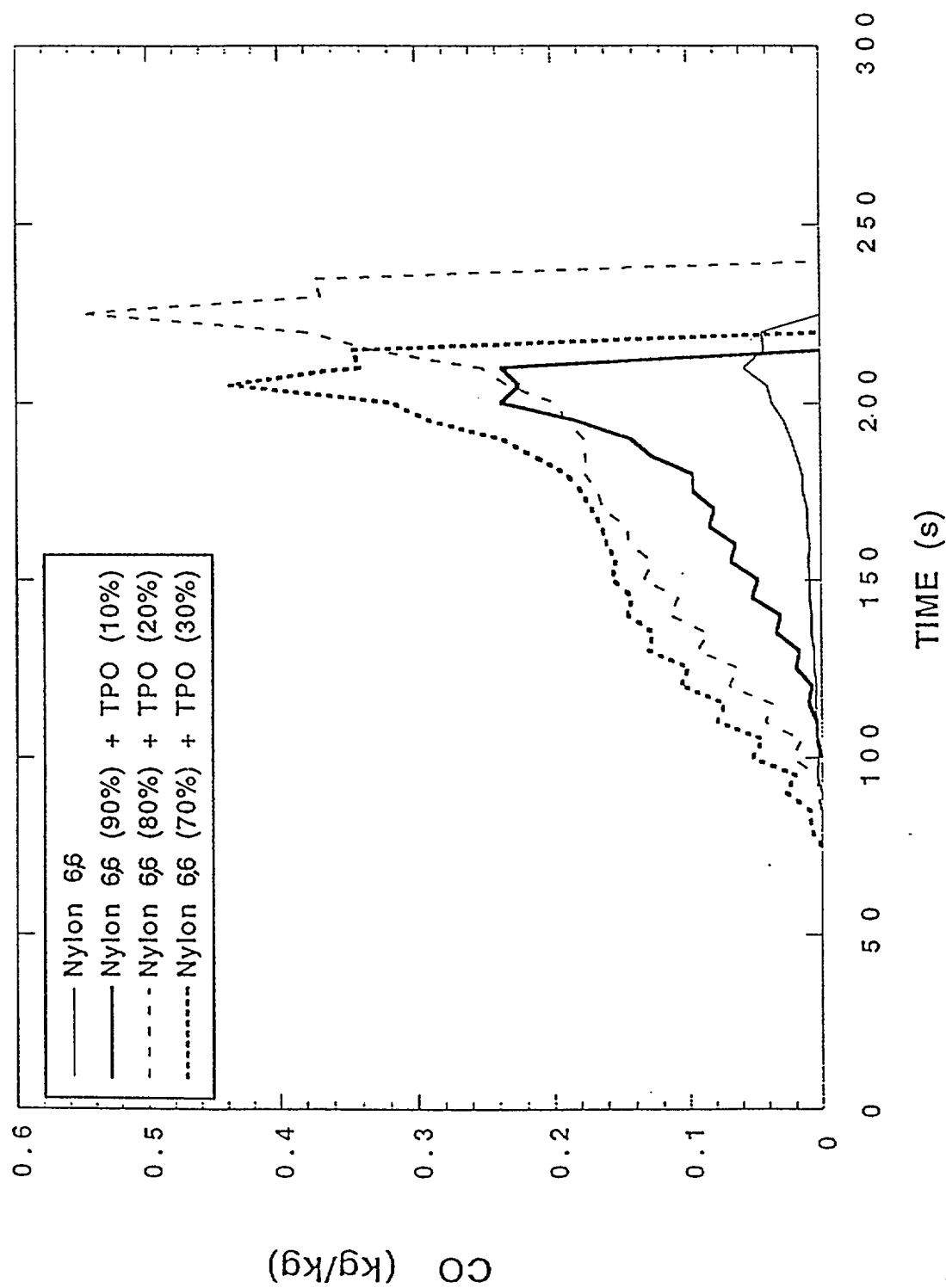


Fig.5 Comparison of CO yield of nylon 6,6 and copolymer samples of nylon 6,6/TPO at external flux of 40 kW/m².

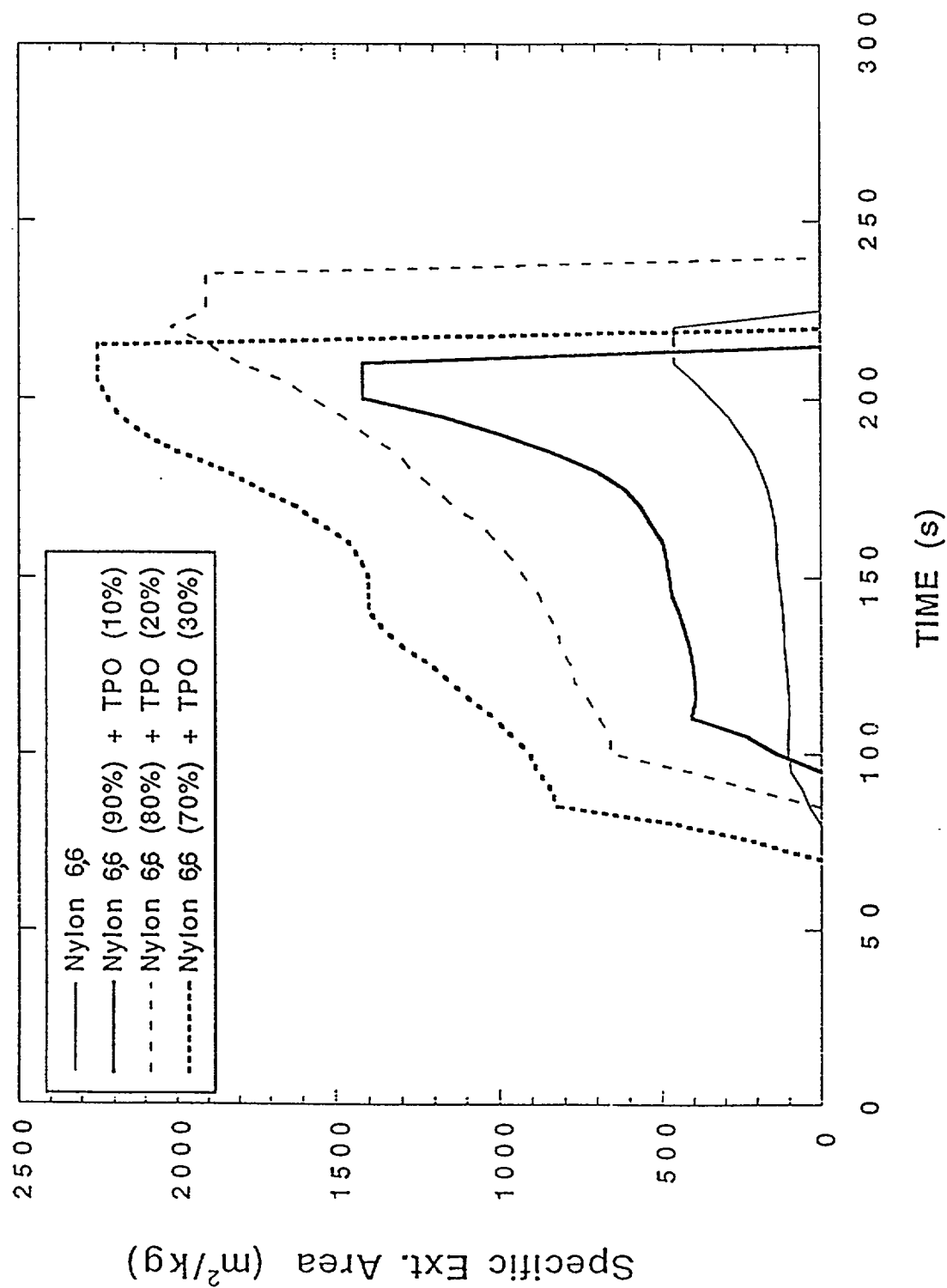


Fig.6 Comparison of specific extinction area of nylon 6,6 and copolymer samples of nylon 6,6/TPO at external flux of $40 \text{ kW}/\text{m}^2$.

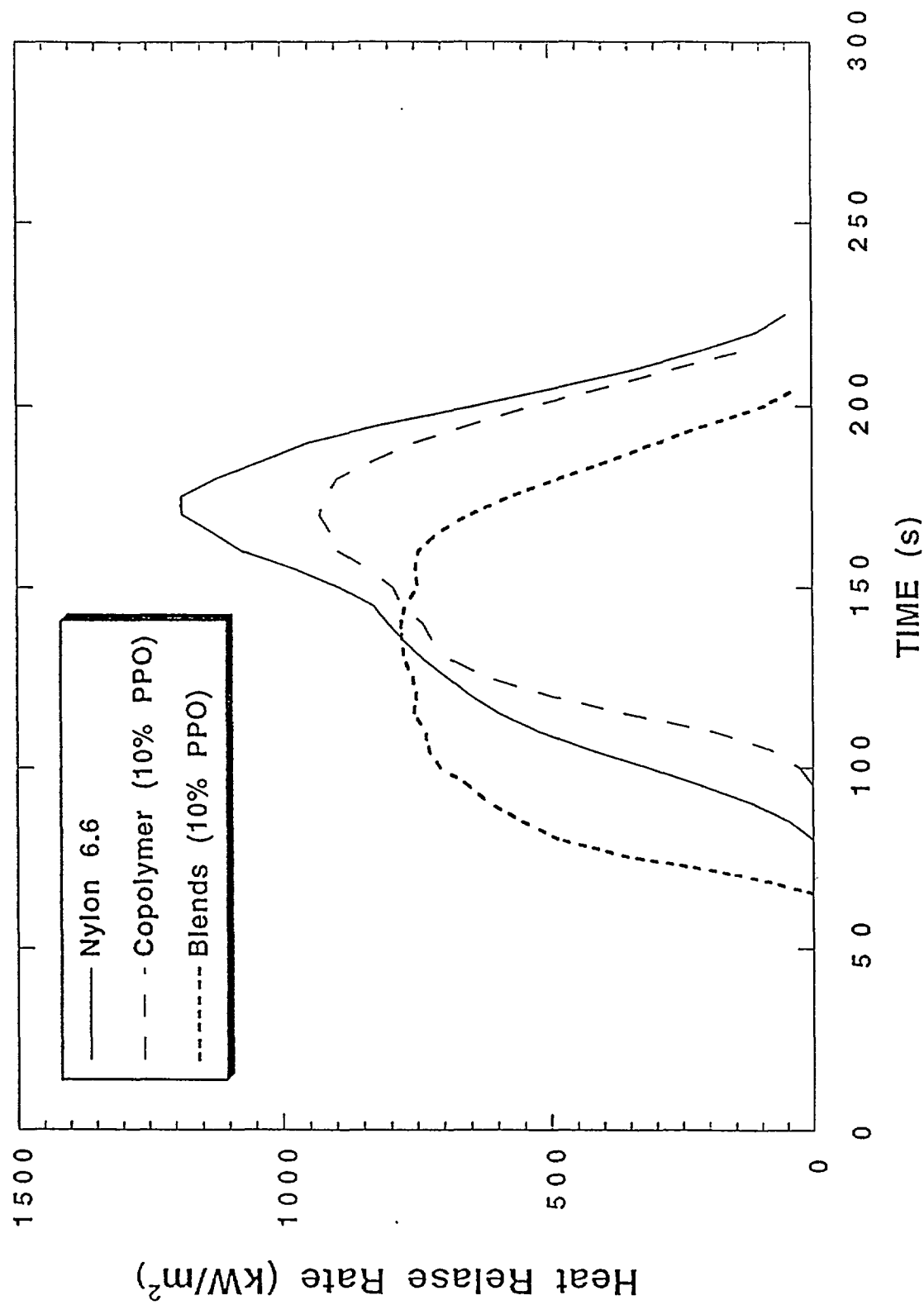


Fig.7 Comparison of heat release rates of nylon 6,6, the blended sample and the copolymer sample of nylon 6,6/TPO at external flux of 40 kW/m².

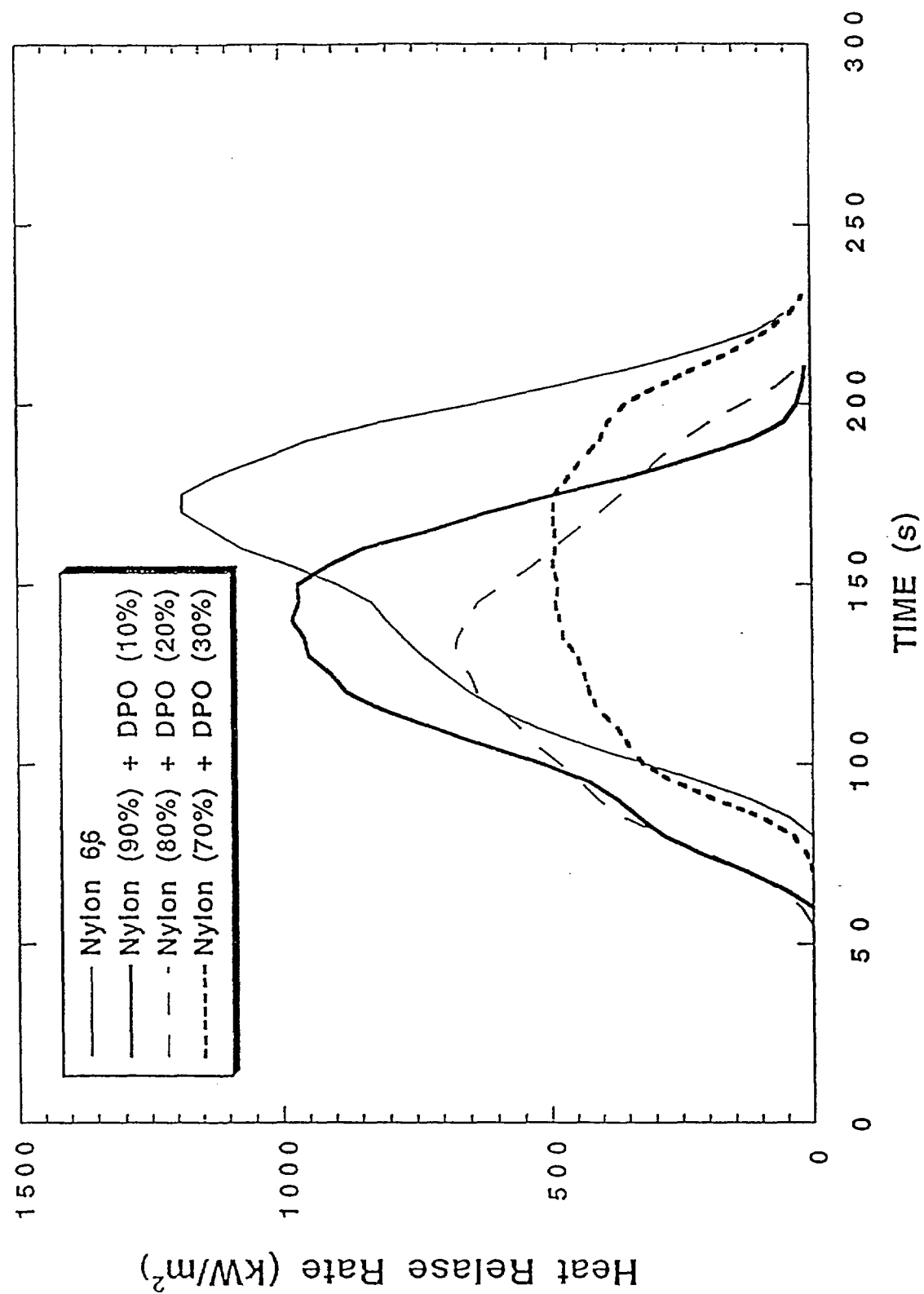


Fig.8 Comparison of heat release rate of nylon 6,6 and copolymer samples of nylon 6,6/DPO at external flux of 40 kW/m^2 .

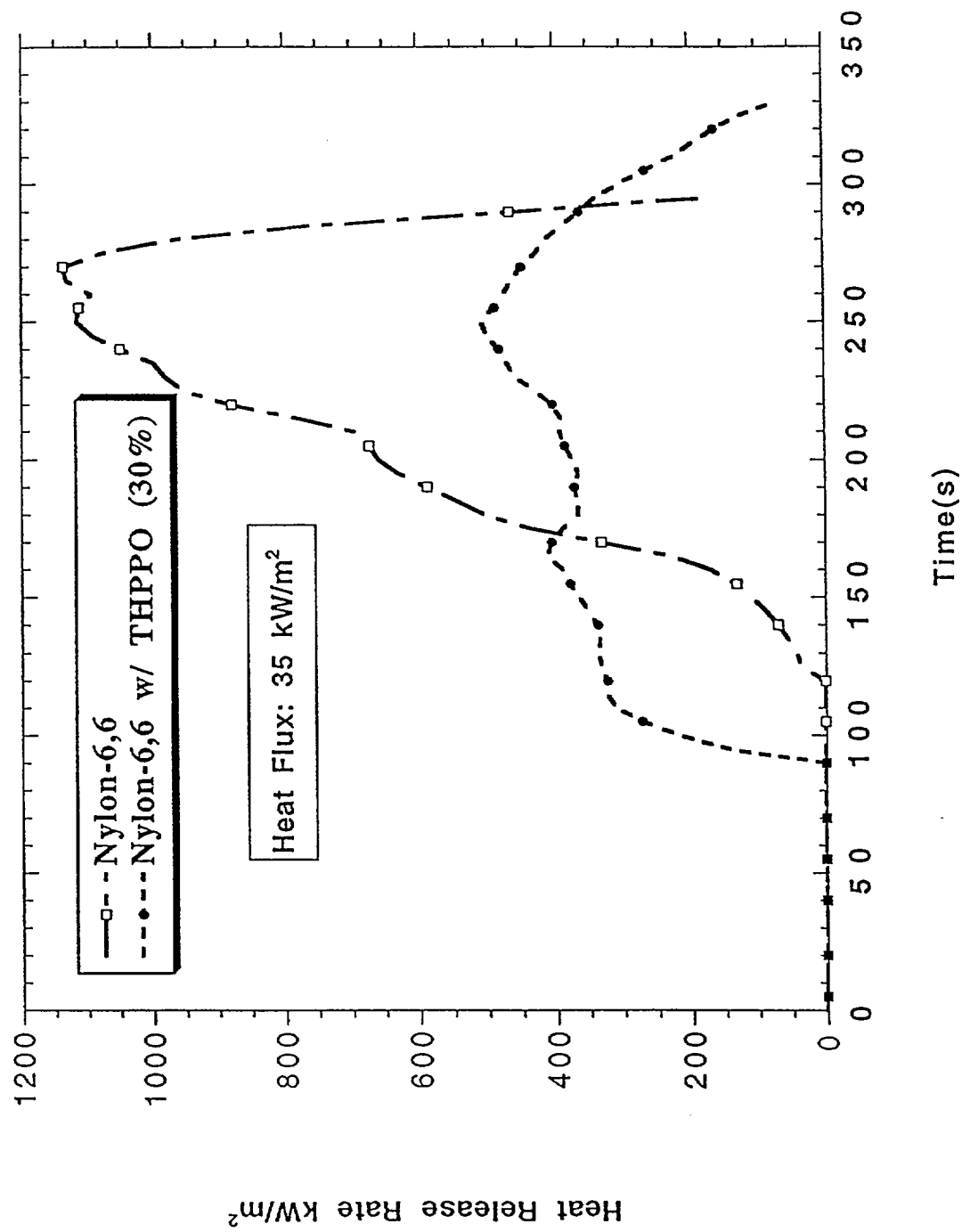


Fig.9 Comparison of heat release rate of nylon 6,6 and the nylon6,6/THPPO(30 weight%) blended sample at external flux of 35 kW/m².

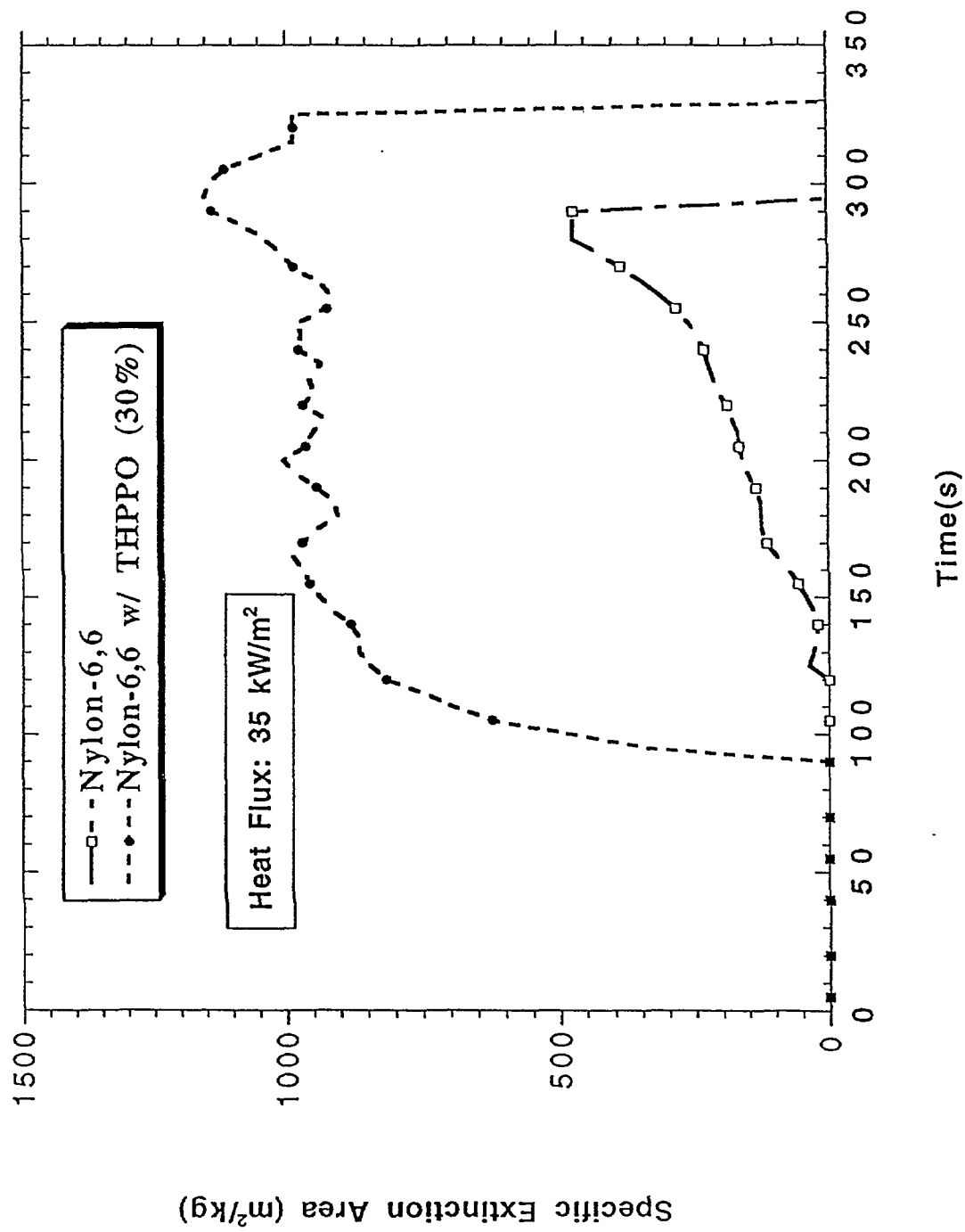


Fig.10 Comparison of specific extinction area of nylon 6,6 and the nylon 6,6/THPPO(30 weight %) blended sample at external flux of 35 kW/m^2 .

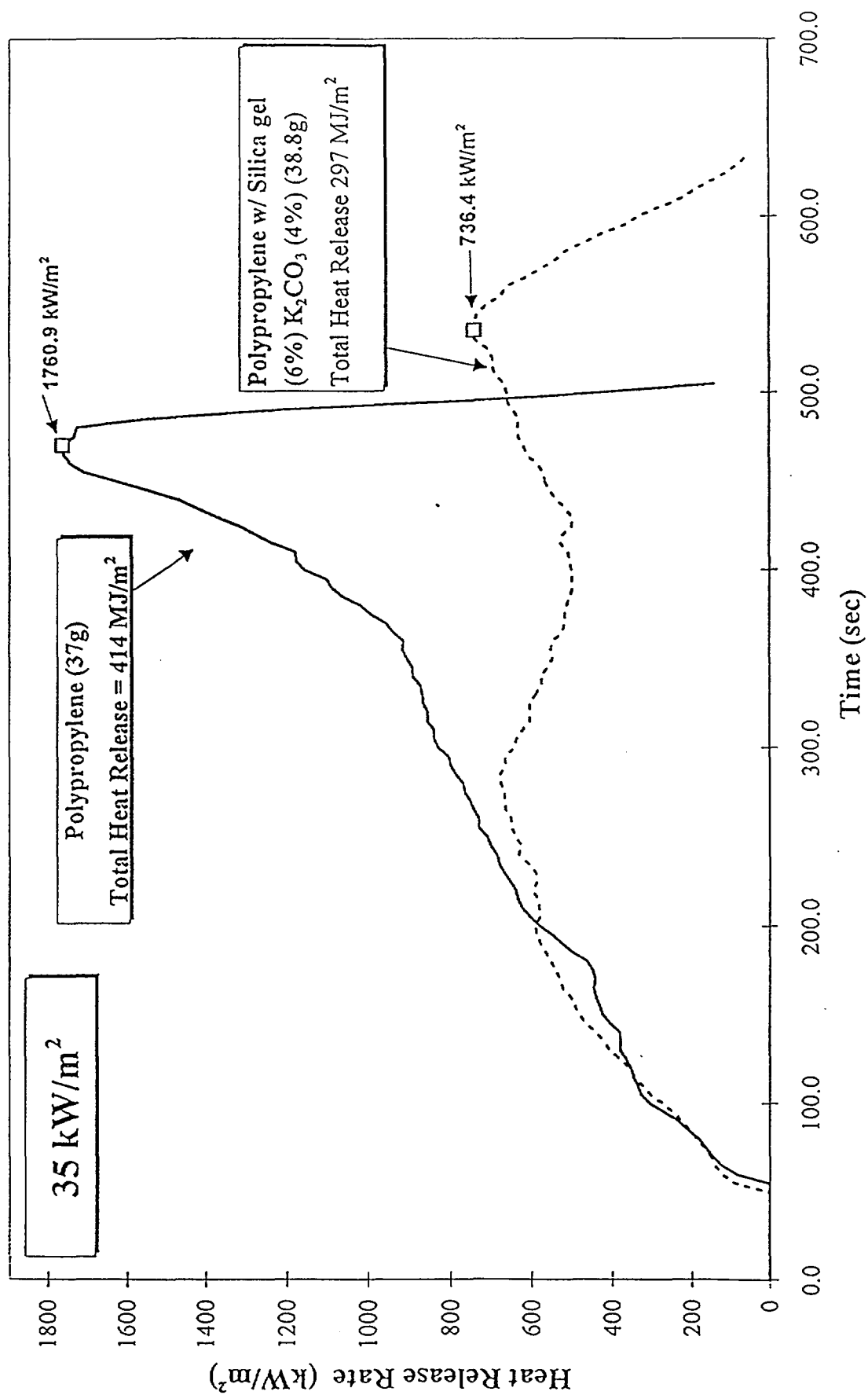


Fig.11 Comparison of heat release rate of PP and PP with silica gel/ K_2CO_3 at external flux of 35 kw/m².

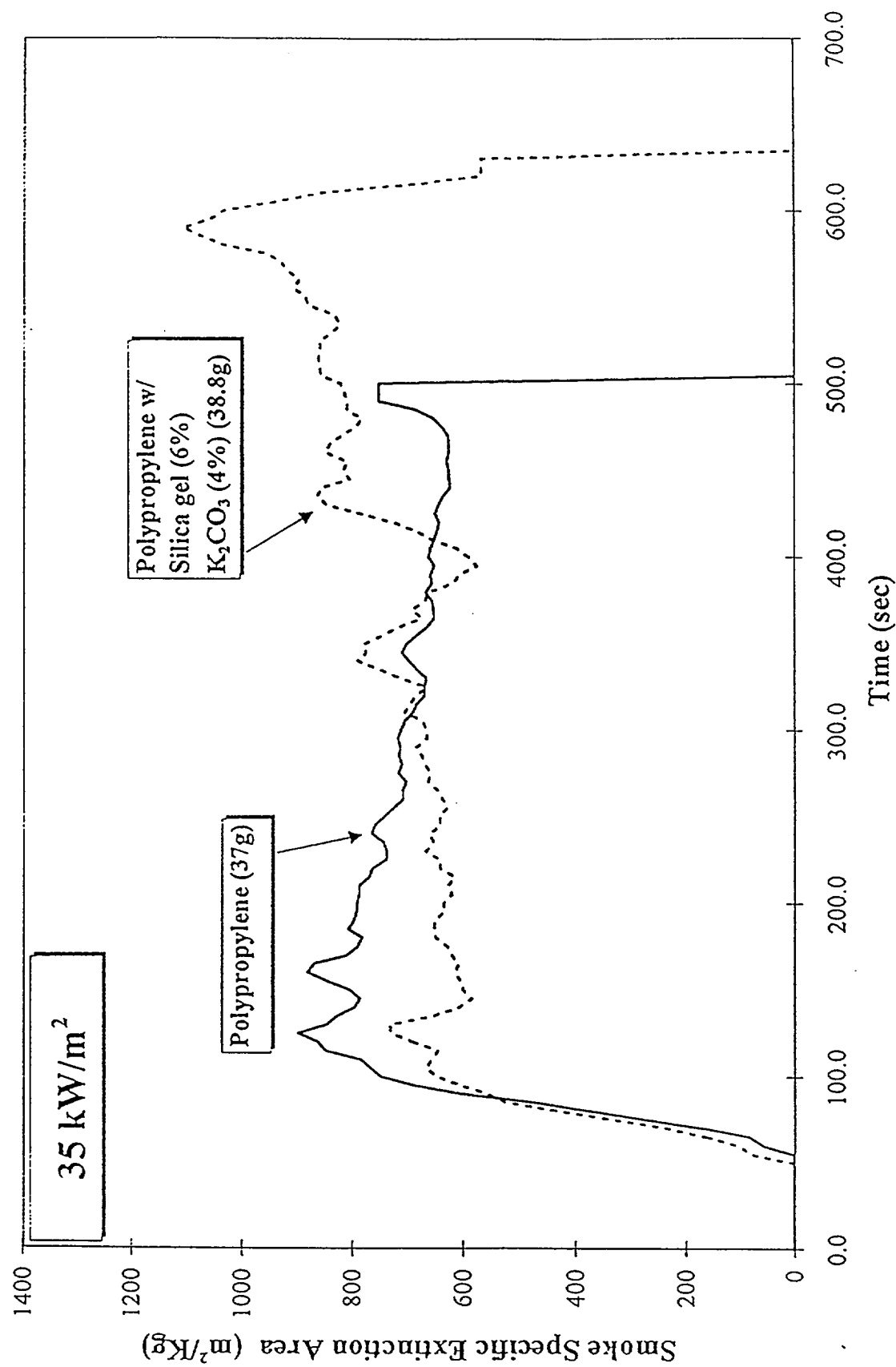


Fig.12 Comparison of specific extinction area of PP and PP/silica gel/ K_2CO_3 at external flux of 35 kW/m^2 .

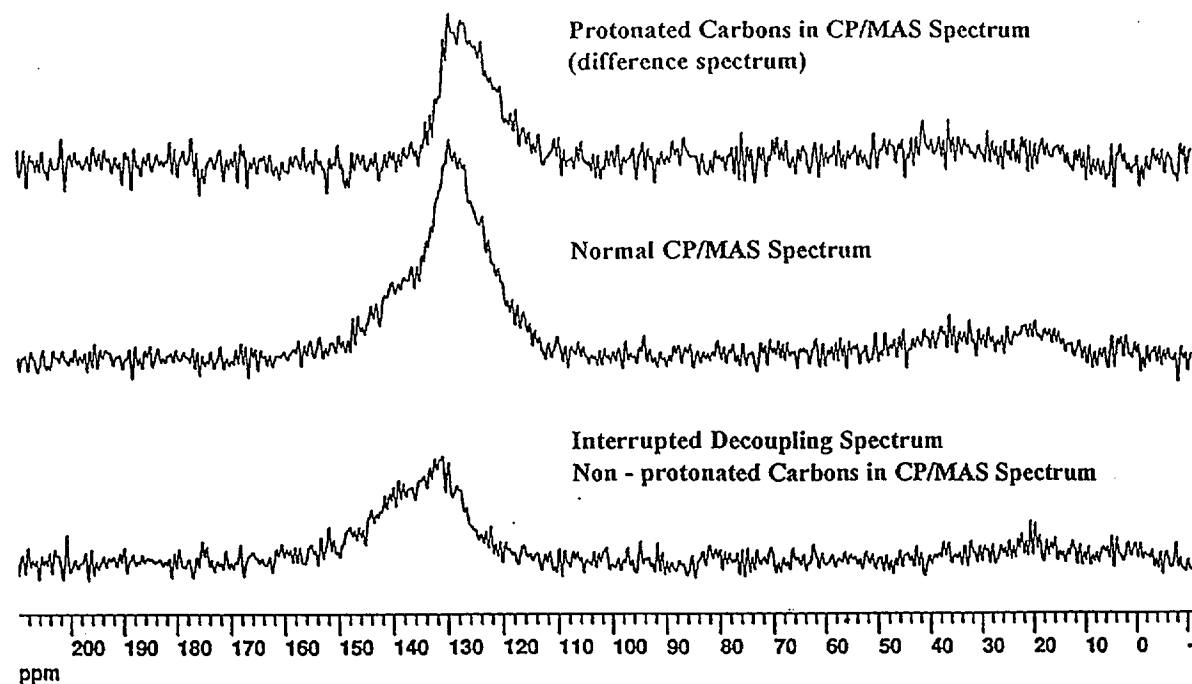


Fig. 13. Solid state ^{13}C NMR spectra of char of PVA with silica gel only (mass ratio: 90:10).

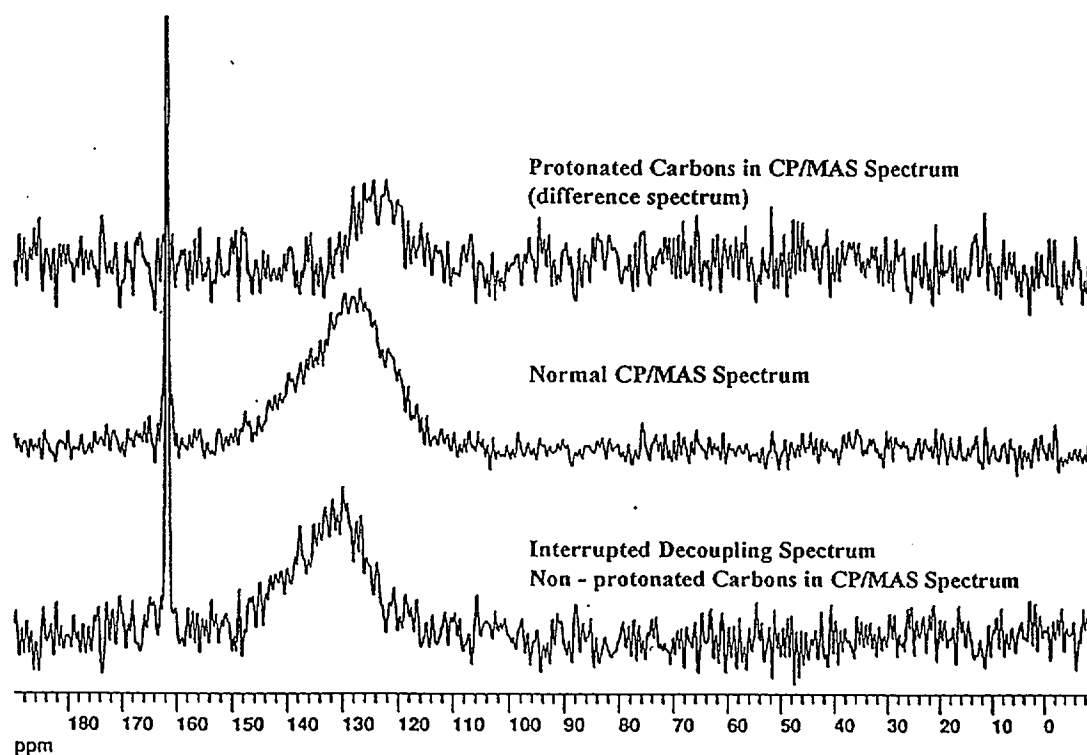


Fig. 14. Solid state ^{13}C NMR spectra of char of PVA with silica gel / K_2CO_3 (mass ratio: 90:6:4).